

Suitability of Thin-Layer Chromatography–Flame Ionization Detection with Regard to Quantitative Characterization of Different Fossil Fuel Products.

I. FID Performances and Response of Pure Compounds Related to Fossil Fuel Products

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Abstract

Controversy exists concerning quantitation using thin-layer chromatography–flame ionization detection (TLC–FID). Inadequate sample selections and detector designs and the non-uniformity of chromarods have been blamed for some confusing results. In this paper, performances of a modern TLC–FID system (which includes the newest detector configuration) are tested on polycyclic aromatic compound standards and related compounds as a preliminary step to evaluate its suitability for quantitative hydrocarbon group type analysis of different coal and petroleum products. Thus, evaluation of performances of the most modern FID configuration is carried out. FID linearity is evaluated as a function of sample load and scan speed for high-molecular-weight and semi-volatile standards. TLC–FID response factors for compounds of several homologous series are studied in order to differentiate effects of volatility from those exclusively due to chemical nature concerning FID response. Therefore, criteria are developed for the accurate application of TLC–FID to fossil fuel samples. Measurements of chromarod temperatures are carried out in order to evaluate whether an evaporation of compounds outside the H₂ flame might take place.

Introduction

Improvements in instrumentation during the last decade have made it possible for thin-layer chromatography (TLC) to be a mature, very useful technique complementary to high-performance liquid chromatography (1). Developed in the 1970s,

TLC with flame ionization detection (TLC–FID, also named Iatroscan) is a technique which combines the advantages of TLC with the possibility of quantitation using FID (2,3). Although certain doubts regarding the acceptability of the quantitative results using this technique have been reported (4–5), there has also been an evolution in instrumentation of TLC–FID. Improvements include the relatively recent changes in detector design in conjunction with the use of automatic sample spotters, advances in technology of chromarod (chromatographic unit) manufacturing, as well as the evolution of electronics for data acquisition and treatment. However, there are little data on detector performance using this configuration (4). Likewise, TLC–FID has been reported to be limited by sample volatility (2), but data concerning the suitability of this technique for polycyclic aromatic compounds (PACs) and related samples (e.g., fossil fuels) using pure standards are scarce. Because of the complexity of coal and petroleum products, these kinds of standards are usually studied prior to the analysis of real samples whenever a chromatographic technique is developed in order to evaluate its suitability.

Although TLC–FID has been applied to mixtures of pure compounds in several fields of chemistry (2), in the field of fossil fuel analysis it is mainly used for hydrocarbon group type analysis (HGTA, also called SARA [Saturates, Aromatics, Resins, Asphaltenes] analysis or compound-class fractionation) (6,7). This characterization involves separation into saturates, aromatics, polars (or resins), and asphaltenes (or uneluates), although the names and nature of fractions vary depending on sample nature and history. These kinds of analyses are important in fossil fuel processing because they allow either the quality of a given product to be monitored or the chemical composition of a given feed to be correlated with its processability and/or the quality of the derived final products.

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Although chromatograms derived from HGTA of different types of fossil fuel samples are similar from a qualitative point of view, each peak in each chromatogram is composed of hundreds of compounds which can be different from one sample to another. As an example, the "aromatic peak" of a heavy oil sample can be very different from the "aromatic peak" of a coal hydroliquefaction product with regard to its components. In fact, the feature common to all fossil fuel samples is that they are composed of hydrocarbon-related products ranging from non-aromatic hydrocarbons to many varieties of PACs. Obviously, all this must affect the FID response of peaks to some extent and, consequently, linearity and quantitation. Apart from the qualitative similarity of chromatograms for fossil fuel products, there seems to be a widespread tendency among researchers to consider FID response for fossil fuel samples as homogeneous for all the peaks. However, the supposed homogeneity in TLC-FID response should be verified for each sample type; therefore, the need of a calibration should not automatically be excluded.

The purpose of this work was to study the suitability of a modern TLC-FID system as an initial step to evaluate the suitability of TLC-FID for rapid and quantitative HGTA of different fossil fuels from petroleum and coal products. First, the performance of the FID detector was evaluated using pure standards related to fossil fuel samples (alkanes, PACs from different families, and some pure fractions from fossil fuels). Therefore, FID repeatability and linearity (as a function of sample load and scan speed) were studied.

Given that a hypothesis of a volatilization of compounds prior to combustion has been reported concerning the use of TLC-FID (4), standards with different volatilities were also studied. Because of the scarcity of data in the literature, flame and chromarod temperatures were measured at different scan speeds in order to evaluate the consistency of such a hypothesis. Response factors for compounds of several homologous series of compounds that are related to coal and petroleum products were also studied in order to differentiate between effects of volatility and those exclusively due to chemical nature. Therefore, the development of criteria was intended for use in the accurate application of TLC-FID to fossil fuel samples.

Experimental

Standards

The studied standards involved *n*-alkanes and PACs, mainly polycyclic aromatic hydrocarbons (PAHs), heteronuclear-PACs, and hydroxy-PACs. They were purchased from Acros Chimica NV (Geel, Belgium). Planar cata-PAHs consisted of toluene ($\geq 99\%$), anthracene ($\geq 99\%$), phenanthrene ($\geq 98\%$), fluoranthene (98%), and chrysene (90–95%). Planar peri-PAHs consisted of pyrene (98%), perylene ($\geq 99\%$), benzo[a]pyrene (98%), and coronene ($\geq 99\%$). Non-planar PAHs consisted of acenaphthene (99%), fluorene (98%), tetralin (technical grade from Scharlau, Barcelona, Spain), 1,2-dihydronaphthalene (96%), 2,3-benzofluorene (90%), and 1,10-dihydroanthracene (90%). Polyphenyls consisted of rubrene (99%). Alkyl-PAH consisted of 2-methylnaphthalene (97%). Hydroxy-PACs consisted of 2-naphthol

($\geq 99\%$), 9-hydroxyfluorene (97%), and 9-phenanthrol (technical grade). Heteronuclear PACs consisted of carbazole (96%), 2-hydroxycarbazole (99%), acridine (98%), 7,8-benzoquinoline (97%), dibenzofuran ($\geq 99\%$), phenoxazine (97%), dibenzothioephene (97%), phenyldisulfide (99%), and tianthrene (97%). *n*-Alkanes consisted of tetracosane (*n*-C₂₄, 99%), docosane (*n*-C₂₂, $\geq 98\%$), nonadecane (*n*-C₁₉, $\geq 99\%$), octadecane (*n*-C₁₈, $\geq 98\%$), hexadecane (*n*-C₁₆, $\geq 99\%$), tridecane (*n*-C₁₃, $\geq 97\%$), dodecane (*n*-C₁₂, $\geq 99\%$), decane (*n*-C₁₀, $\geq 99\%$), and octane (*n*-C₈, $\geq 99\%$).

Data of volatility for these compounds were mainly found in the Thermodynamics Research Center database (Texas A&M University, College Station, TX). Some fractions (saturates and aromatics) obtained using medium-pressure liquid chromatography (MPLC) from a heavy oil were also used as standards. Details about the chromatographic isolation, as well as characteristics of the fractionated heavy oil, were reported elsewhere (7).

TLC-FID experiments

Sample application (0.2–2 μ L) was carried out using a 3202/IS-02 automatic sample spotter (SES, Bechenheim-Alzey, Germany). Chromatographic separation was performed on S-III chromarods (silicagel, 5- μ m particle size, 60- \AA pore diameter, Iatron Labs, Tokyo, Japan). Quantitation of peaks was carried out using an Iatroscan Mark 5 TLC-FID apparatus (Iatron Labs). In this detector configuration, the ion collector is closer to the chromarods than it is in the older models.

Acquisition and treatment of data were carried out using a data acquisition card and Boreal software (JMBS Development, Grenoble, France). Raw chromatograms were transferred for further treatment to LabCalc (Bomem, Quebec, Canada) software, which allows for baseline corrections.

A strict operating procedure, which includes details which affect repeatability (i.e., chromarod conditioning, blank scanning, verification of complete combustion, etc.), was previously published (7) and used throughout this work. Hydrogen and oxygen flows were 160 mL/min and 2100 mL/min, respectively, as suggested in the literature (2).

A usual experiment involved the following steps. Standards were solubilized in CH₂Cl₂. Samples were freshly prepared or stored in a freezer under argon. Sets of 10 chromarods were pre-assembled in a frame. After sample application, they were developed using dichloromethane-methanol (DCM-MeOH 95%, v/v) for 5 min. Finally, chromarods were sequentially passed through the H₂ flame of the Iatroscan FID for quantitation of peaks at 30 s/scan unless otherwise stated.

The amounts (μ g) reported throughout the text correspond to the mass effectively applied. The sample load range studied for the standards was 0.1–12 μ g. The response factor of each standard is defined as its corresponding area (counts in μ V/s) per mass unit (μ g). Only the absolute response factors are used throughout this paper.

Measurements of chromarod and flame temperatures

Temperature measurements were made using a data acquisition system consisting of a thermocouple (Thermocoax, Suresnes, France, type S, 1-mm diameter, 0–1700°C range), a Fluke (Everett, WA) Hydra 2620 multichannel data acquisition unit, and a Hewlett-Packard (Palo Alto, CA) HP-95 hand-held

computer that received and stored the data. A serial RS-232-C connection was used to send the data from the data acquisition unit to the computer. The rate of data acquisition was 1 temperature measurement per second.

The thermocouple was put into contact with the chromarod surface at a 90° angle and fixed in this position using glue in order to avoid the presence of air between the surface and the

thermocouple as much as possible. The flame went directly through this connection; the FID assembly is the moving element in the Iatroscan apparatus, so thermocouple and chromarod did not move during the experiment. The glue was burned by the H₂ flame the first time, but after the glue flame was extinguished, the connection remained and became resistant to burning. It was possible to perform several temperature determinations with the H₂ flame passing through the connection without problem.

Results and Discussion

Repeatability of FID experiments

First, FID performance was evaluated with regard to repeatability of experiments. Relative standard deviation (%RSD) of the absolute response factors was calculated for each standard studied at the same sample load (5 µg) (Table I). %RSD is defined here as

$$\%RSD = \frac{(\sigma \times 100)}{\mu} \quad \text{Eq 1}$$

where σ is the sample standard deviation and μ is the average of response factors (in this case) of five measurements.

In general, %RSD was lower than 5% regardless of the values of vapor pressure (at a given temperature) of the compounds studied. It should be mentioned that several compounds with relatively high volatilities are included in Table I (i.e., acenaphthene, phenanthrene, and 2-methylnaphthalene). It should be taken into account that a %RSD of approximately 5% is common in analytical practice (2). Figure 1 plots the variation of %RSD for rubrene and *n*-tetracosane loads. The lowest sample loads (0.1 µg) gave the highest %RSD (11%), which is in agreement with the literature. Nevertheless, a %RSD as high as 55% was reported for an approximately 0.1-µg sample load using an older Iatroscan technology (manual spotting, Mark III FID configuration, and S-II chromarods) (2). In the present case, sample loads higher than 0.5 µg gave (in general) a %RSD lower than 5.

Evaluation of FID linearity with sample load and scan speed for quantitative purposes

When area counts (*A*) from a chromatographic detector can be linearized against sample load (*m*) with adequate regression coefficients for a given compound, the slope of the regression represents the theoretical response factor (*A/m*) of the compound. In the case of an ideal linear detector, this response factor should be constant regardless of the sample load. However, among the detectors commonly considered as linear, slopes vary for each different compound to an extent dependent on each particular detection system. Therefore, a calibration step is usually needed.

Given that one of the aims of this work was to evaluate the performance of TLC-FID technique without interferences related to the inherent volatility of the solute, rubrene was chosen to

Table I. Repeatability of PACs and Related Standards Expressed as %RSD

Standard	%RSD
Rubrene	2.39
Anthracene	4.17
Phenanthrene	2.98
Fluoranthene	4
Chrysene	2.91
Pyrene	4.93
Perylene	3.86
Benzo[a]pyrene	1.27
Coronene	5.1
Acenaphthene	4.17
Fluorene	3.36
1,2-Dihydronaphthalene	5.4
2,3-Benzofluorene	2.85
2-Methylnaphthalene	6.2
Carbazole	2.19
2-Hydroxycarbazole	4.08
Acridine	0.84
7,8-Benzoquinoline	3.07
Dibenzofuran	5.14
Phenoxazine	2.73
Dibenzothiophene	2.61
Phenyldisulfide	2.03
Tianthrene	2.67
2-Naphthol	5.23
9-Hydroxyfluorene	5.48
9-Phenanthrol	1.67
Tetracosane	4.21
1,2-Dihydroanthracene	4.36

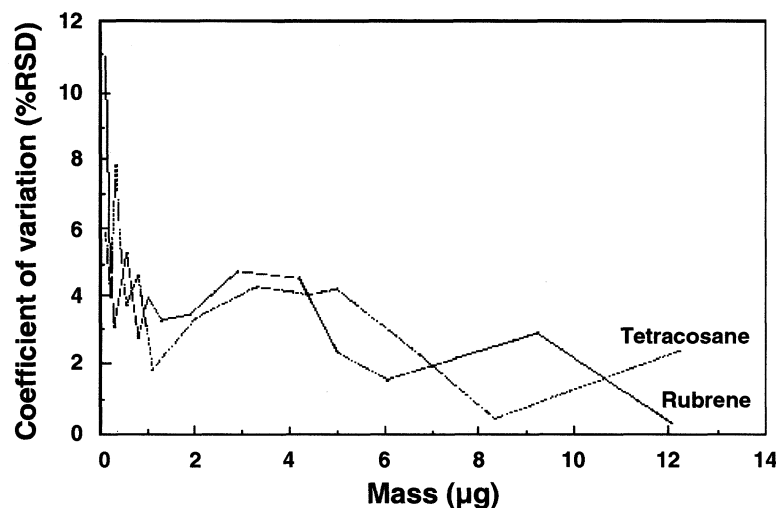


Figure 1. Evolution of %RSD with sample load for *n*-tetracosane and rubrene.

Table II. Fitting of Experimental Data for Different Rubrene Loads

Rubrene sample			Linear regression*		Logarithmic regression†		
Mass (µg)	Area	Response factor‡	Calculated area§	Error %	Log area	Calculated log area**	Error %
0.2	170.9	0.730	197.5	-15.55	2.233	2.291	-2.61
0.5	414.4	0.885	448.8	-8.3	2.617	2.618	-0.03
0.75	644.7	0.918	700.1	-8.59	2.809	2.809	0.01
0.95	829.8	0.887	951.3	-14.64	2.919	2.944	-0.86
1.0	1110.7	1.112	1019	8.25	3.046	2.946	2.31
1.2	1218.9	1.042	1203	1.31	3.086	3.049	1.19
2.0	2214.6	1.108	2092	5.53	3.345	3.302	1.29
3.0	2970.1	0.991	3165	-6.56	3.473	3.493	-0.57
4.0	4308.7	1.078	4237	1.66	3.634	3.629	0.15
5.0	5526.3	1.106	5310	3.91	3.742	3.734	0.22
6.0	6599.5	1.101	6383	3.28	3.820	3.819	0.02
7.0	7297.4	1.044	7456	-2.17	3.863	3.892	-0.75
8.0	8383.8	1.049	8526	-1.7	3.923	3.955	-0.81

* $A = 1074 \times m - 53.79$ (correlation coefficient $r = 0.9990$).
† $\log A = 1.084 \times \log m + 2.976$ (correlation coefficient $r = 0.9979$).
‡ Response factor expressed as $A/(m \times 1000)$.
§ Calculated area defined as values obtained with linear regression equation.
** Calculated log area defined as values obtained with logarithmic regression equation.

Table III. Area Mass Regressions Obtained for Different Standards

Sample	Linear regression*	Logarithmic regression
Phenanthrene	$A = 677.5 \times m - 228.7$ ($r = 0.9977$)	$\log A = 1.105 \times \log m + 2.719$ ($r = 0.9990$)
Tetracosane	$A = 663.4 \times m - 19.26$ ($r = 0.9977$)	$\log A = 0.9363 \times \log m + 2.849$ ($r = 0.9973$)
Benzo[a]pyrene	$A = 975.9 \times m - 111.5$ ($r = 0.9986$)	$\log A = 1.0747 \times \log m + 2.927$ ($r = 0.9973$)
Fluorene	$A = 573.0 \times m - 102.0$ ($r = 0.9934$)	$\log A = 1.144 \times \log m + 2.629$ ($r = 0.9972$)
Fluoranthene	$A = 886.0 \times m - 390.5$ ($r = 0.9977$)	$\log A = 1.148 \times \log m + 2.796$ ($r = 0.9991$)
Pyrene	$A = 761.2 \times m + 205.4$ ($r = 0.9905$)	$\log A = 1.0747 \times \log m + 2.895$ ($r = 0.9925$)

* Abbreviations: A, area counts; m, mass of standard PAC; r, correlation coefficient.

It can be seen that both linear and logarithmic regressions show adequate regression coefficients (even in the cases of more volatile compounds studied, such as fluorene and phenanthrene), although logarithmic regressions provide smaller errors at low sample loads. Likewise, intercepts from logarithmic regressions are nearer to zero than those from linear regressions, which has more physical meaning than intercepts from linear regressions. The general equation for chromatographic detection is

$$A = a \times c^b \quad \text{Eq 4}$$

where c is the concentration and a and b are constants of each detection system, as proposed by Fowles and Scott (8). According to this equation, there has been no detector manufactured as of yet that has a value of b equal to unity over more than two orders of concentration range. From the point of view of quantitative accuracy, b does not have to be equal or close to unity, providing an accurate value of b is known (8).

A particular capability of TLC-FID is the ability to vary the scan speed. Figure 2 shows the variation of the response factor versus rubrene load at five different scan speeds. Table IV shows error percentages (as previously defined) from linear and logarithmic regression curves for the different scan speeds studied. As scan speed decreases, FID response also decreases and a greater deviation from the linearity for sample loads lower than 1 µg was found.

In Figure 2, it is shown that results using 30 or 35 s/scan speeds are almost indistinguishable. However, it can be seen that FID response versus rubrene load at slow speeds (50 and 60 s/scan) are also linear, although these scan speeds provide smaller signals. Therefore, a slow scan speed can be used to reduce sensitivity in order to avoid saturation problems in some particular cases.

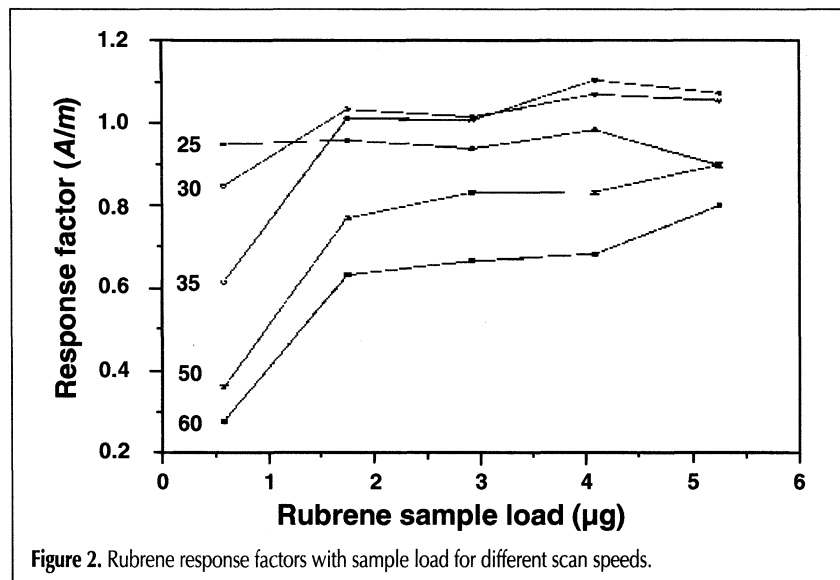
study linearity in depth. This standard has a high molecular weight (MW= 532) and low volatility (i.e., 6.373×10^{-6} mm Hg at 171°C). Evaluation of detector linearity with respect to sample load is presented in Tables II and III for rubrene and other semi-volatile and non-volatile standards. Error was calculated in Table II for each experimental point as

$$\text{Error \%} = ([A - A_c]/A) \times 100 \quad \text{Eq 2}$$

in the case of the linear regressions and as

$$\text{Error \%} = ([\log A - \{\log A\}_c]/\log A) \times 100 \quad \text{Eq 3}$$

in the case of the logarithmic regressions, where A_c and $(\log A)_c$ are the values of A and $\log A$ calculated using the corresponding fitting curve.



The effect of the significantly lower response at the lowest scan speed (60 s/scan), which occurs at each mass studied, should be explained according to combustion/volatilization/ionization mechanisms in the H₂ flame, which are poorly understood for TLC-FID system. Karlsen and Larter (9) reported that response is decreasing at 30 s/scan and falling to a minimum (up to 50%) between 40 and 50 s/scan because of volatilization losses for several standards. According to the authors, this happened before an increase of the response at even slower scan speeds. This last effect was attributed to a more effective ion formation because of the higher temperature reached on chromarods at slower scan speeds. The minimum of the curve is therefore interpreted to reflect the intercept of the two response influence mechanisms. This means that the Iatroscan used in that work gave non-uniform response factors along the scan speed range. However, our experimental results are in disagreement, as can be seen in Figure 2 and as previously mentioned. Discrepancy in results could be caused by the use of different Iatroscan systems throughout the respective works (Mark IV FID configuration in the work of Karlsen and Larter) and, above all, to the inherent volatility (vapor pressure) of the standards studied in each case (details about standards and sample loads used for evaluating the variation of response with scan speed were not given in that work). It should be remembered that a high-MW standard (rubrene) was used in our work in order to distinguish the performance of the technique on its own and the effect of the sample volatility. According to our results concerning the evolution of rubrene response in function of scan speed, no significant loss of signal at 25, 30, and 35 s/scan was found, although response is progressively smaller as scan speed decreases (50 and 60 s/scan).

Figure 2. Rubrene response factors with sample load for different scan speeds.

Table IV. Error Percentage of Linear and Logarithmic Regression for Different Scan Speeds

	Mass	Scan speed (s/scan)				
		25	30	35	50	60
Linear regression	0.6	-4.69	-11.93	-36.94	-61.55	-48.67
	1.8	1.32	0.48	-0.72	-3.7	-5.2
	2.9	0.14	-2.95	-4.65	-1.54	-7.36
	4.1	5.22	1.64	3.23	-3.45	-7.73
	5.3	-3.59	-0.06	-0.32	3.02	-6.54
Regression coefficient*		0.9979	0.9996	0.9984	0.9974	0.9923
Logarithmic regression	0.6	-0.16	-0.45	-1.23	-2.08	-2.08
	1.8	0.16	0.8	1.88	2.8	3.07
	2.9	-0.06	-0.13	0.05	0.86	0.44
	4.1	0.55	0.1	0.12	-0.81	-1.17
	5.3	-0.51	-0.35	-0.96	-1.09	-0.6
Regression coefficient		0.9993	0.9993	0.9967	0.9942	0.9946

* Regression coefficient obtained in the mass range 0-5.3 µg.

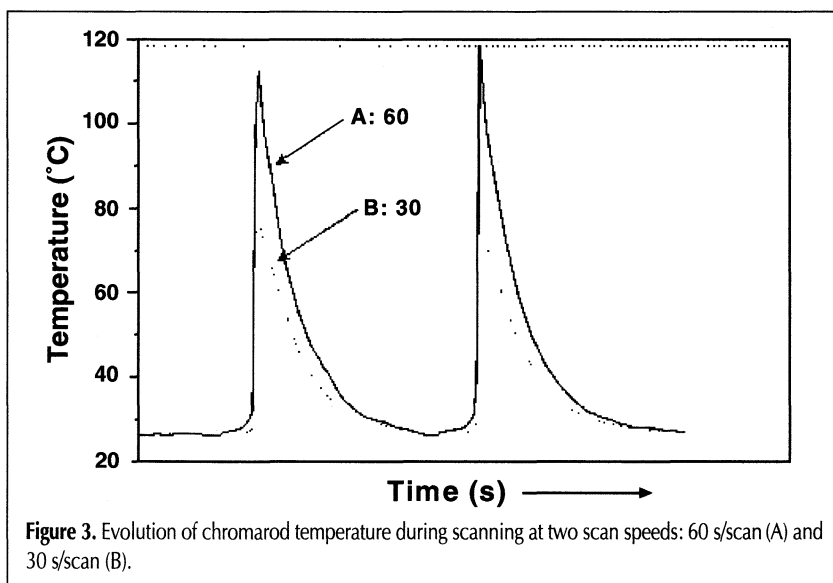


Figure 3. Evolution of chromarod temperature during scanning at two scan speeds: 60 s/scan (A) and 30 s/scan (B).

Several experiments were carried out in our laboratory in order to evaluate whether volatilization may effectively take place prior to sample combustion. Ranny (2) reported that volatilization prior to combustion takes place when analyzing a mixture of mono- and tripalmitates. However, he pointed out that the degree of evaporation outside the detector depends not only on the flame temperature and chromarod conductivity but also on the volatility of samples. Data on chromarod temperature are scarce in the literature. As far as we know, only an estimation of chromarod conductivity from the conductivity of glass and some measurements of chromarod temperature without detail have been reported (2). Figure 3 shows the evolution of chromarod temperatures during scanning at two scan speeds

which were measured according to the procedure described in the Experimental section. This figure shows an increase in chromarod temperature with a decrease in scan speed. However, the difference is only approximately 20°C when passing from 30 to 60 s/scan. This difference does not seem to justify the previously mentioned difference in response in the case of rubrene, which presents a limited volatility even at 230°C (1.05×10^{-3} mm Hg). Likewise, it should be mentioned that the maximum temperature on a chromarod is reached from room temperature in a short period of time (2 s) regardless of the scan speed. This temperature-time pattern is the same regardless of the scan speed. Given that rubrene is hardly volatile at working temperatures, it seems unlikely to have a significant volatilization prior to combustion in this case. However, another hypothesis that might also explain the observed loss in sensitivity is presented in the next section.

Another reported problem when dealing with Iatroscan, such as a supposed influence of peak shape on TLC-FID response (4), could be caused by sample volatility or the use of old FID configurations or both. The FID response of some lipids has been reported to be affected by the shape of the peaks. For a pure compound, differences in peak response have been reported depending on the development conditions that affect the spread of the sample (4). According to the chromatography theory, the different shapes of a peak obtained by different development lengths must not influence integration. The problem was attributed to non-uniformity of chromarods or detector configuration or both. Likewise, it should be taken into account that, when this problem was reported, several different detector configurations, sample application techniques, and data acquisition systems were used simultaneously. The existence of this problem was tested in a previous paper using the modern Iatroscan technology described in this work (7). Thus, a polar fraction from a petroleum residue obtained using MPLC was applied on five chromarods and developed to five different lengths using DCM. No significant variation of FID response in relation to development length was found therein. Here, a confirmation of this result is presented in the case of rubrene. Figure 4 shows area counts of rubrene peaks developed at four different lengths, with the same result as previously mentioned. Differences in integration values are in agreement, taking into account the values of %RSD. This means that the problem can be attributed to older Iatroscan systems or physico-chemical properties of the analyzed solutes rather than the Iatroscan system used throughout this work.

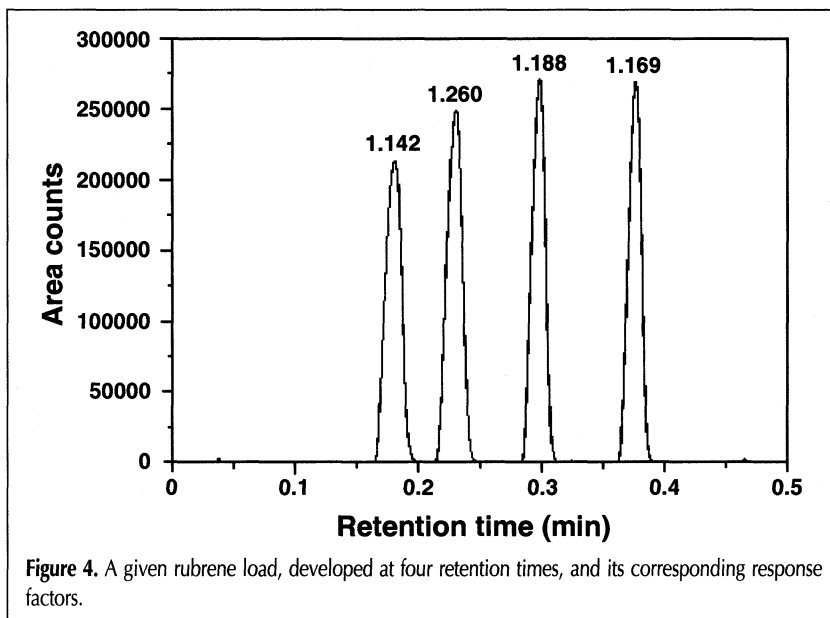


Figure 4. A given rubrene load, developed at four retention times, and its corresponding response factors.

Table V. TLC-FID Response Factors for Different Alkanes

Sample alkanes	Atoms of carbon	Vapor pressure (mm Hg)	Response factor (A/m)
DAO	C ₃₂₊		0.801
Tetracosane	C ₂₄	0.1 (150°C)	0.718
Docosane	C ₂₂	0.313 (150°C)	0.575
Nonadecane	C ₁₉		0.522
Octadecane	C ₁₈	3.496 (150°C)	0.509
Hexadecane	C ₁₆	10.38 (150°C)	0.311
Tridecane	C ₁₃		0.166
Dodecane	C ₁₂		0.090
Decane	C ₁₀		0.033
Octane	C ₈		0.030

Table VI. TLC-FID Response Factors for Different PAHs

Planar PAHs	Number of rings	Vapor pressure (mm Hg)	Response factor (A/m)
DAO	> 6	–	0.949
Rubrene	8	6.373×10^{-6} (171°C)	1.099
Coronene	7	1.629×10^{-5} (150°C)	1.235
Benzo[a]pyrene	5	1.369×10^{-5} (105°C)	1.022
Perylene	5	3.12×10^{-6} (100°C)	0.914
2,3-Benzofluorene	4	–	1.022
Chrysene	4	1.072×10^{-5} (105°C)	0.907
Fluoranthene	4	17.61 (220°C)	0.851
Pyrene	4	13.79 (230°C)	0.833
Anthracene	3	44.85 (221°C)	0.779
Phenanthrene	3	0.6872 (108°C)	0.712
Naphthalene	2	–	0.077
2-Methylnaphthalene	2	44.31 (141°C)	0.179
Toluene	1	–	0.014
Non-planar PAHs			
1,10-Dihydroanthracene	2	–	0.643
Fluorene	2	3.592 (119°C)	0.63
Acenaphtene	2	3.371 (105°C)	0.546
Tetrahydronaphthalene	1	–	0.046

Table VII. TLC-FID Response Factors for Different Heteronuclear PACs

Heteronuclear PAC	Heterocycle type	Vapor pressure (mm Hg)	Response factor (A/m)
Carbazole	N		0.786
2-Hydroxycarbazole	N		0.851
Acridine	N	0.459 (115°C)	0.826
Benzoquinoline	N	3.93×10^{-4} (30°C)	0.732
Phenanthroline	N		0.950
Dibenzothiophene	S		0.603
Thianthrene	S		0.589
Phenyldisulfide	S		0.554
Thionaphthene	S		0.047
Phenoxazine	N,O		0.704
Naphthol	OH	11.1 (150°C)	0.596
9-Phenanthrol	OH		0.841
9-Hydroxyfluorene	OH		0.623
Dibenzofuran	O	6.44 (120°C)	0.467

comparisons should be made with caution between data from Tables V–VII and chromarod temperatures.

Absolute response factors for a long-chain paraffinic and an aromatic fraction, both from a heavy petroleum residue (DAO, with a boiling point higher than 495°C), are also included in Table V. Within the alkane homologous series (Table V), the higher the number of carbons, the higher the response factor for the studied compounds. *n*-Tetracosane presents a response factor closer to that of the alkane fraction from the heavy oil studied. A possible explanation is that, up to C₂₂, alkanes present relatively high values of vapor pressure. Thus, volatilization of these compounds may occur rather than an effective ionization. A similar behavior can be observed in the case of the series of planar PAHs. Table VI

gives the response factors for planar PAHs which are classified according to number of rings, which in turn is related (to some extent) to their vapor pressure at a given temperature.

Absolute response factors are similar and nearly equal to 1 from 4-ring (chrysene) to 8-ring PAHs (differences are not significant, given the %RSD of each compound). However, for 4 or fewer rings, the response factors progressively decrease. This decrease is dramatic when passing from phenanthrene to naphthalene. Likewise, hydrogenated, small-sized, non-planar PAHs that present high values of vapor pressure also have lower response factors. As seen in the evaluation of FID linearity, volatility does not seem to give a complete explanation of the data. A complementary explanation in both cases could take into account that the smaller the compound to be detected and the lower the scan speed, the more complete its combustion will be and the smaller the probability of ions being detected by the FID detector. This effect could also contribute to the decrease in sensitivity and does not depend on the vapor pressure properties of the product. In summary, response factors are reasonably uniform in the case of each chemical family for alkanes longer than C₂₄ and aromatics with 4 or more rings.

With regard to heteronuclear compounds, it is known that their response to gas chromatography (GC)-FID can be expected to be lower than those of the corresponding alkanes or PAHs. Concluding that heteronuclear compounds or even polar fractions from heavy oils and related products should also give a lower response in TLC-FID is not justified. Several additional points should be taken into account in this case, including effects from differences in volatility or even the fact that relative responses of polars and aromatics were reported to vary with the hydrogen flow in the Iatroscan system when the flows are higher than in GC (9).

In the case of model compounds, we generally observed lower responses than those obtained for their hydrocarbon analogues. The low response factors of 2-naphthol, dibenzofuran, and thionaphthene could also be attributed to their relatively high values of vapor pressure, but it seems difficult to distinguish between the effects of volatility and molecular structure. In any case, response factors obtained for non-volatile heteronuclear and phenolic standards are, in general, lower than those obtained for

Table VIII. Response Factors of Fractions from DHO*

Mass (µg)	Saturates	Aromatics	Mass (µg)	Polars
21.0	1.109	0.951	3.2	0.914
16.0	1.124	1.065	3.0	0.954
10.0	1.120	0.922	2.5	0.992
5.0	1.204	1.270	1.6	0.928

* Isolated using MPLC.

Absolute response factors of the standards studied

Results presented here demonstrate the adequate performance of the TLC-FID system studied. Given that our research interest is devoted to quantitative analysis of coal and petroleum products, standards related to those found in fossil fuels were used here to estimate volatility limits for the quantitative application of this technique. The standards studied include PAHs, heteronuclear polycyclic compounds, hydroxy-PACs and alkanes (which appear in petroleum samples together with PACs). Given that the FID response of different chemical families depends (to some extent) on their chemical nature, discrimination between this effect and a possible volatilization must be made when comparing responses. To achieve this discrimination, physico-chemical properties of each standard must be considered with regard to the analytical conditions, and comparisons with responses of non-volatile standards and heavy fossil fuel fractions corresponding to the same chemical family (homologous series) must be performed. With regard to analytical conditions in general, boiling point and molecular weight are used to consider sample volatility. However, these properties are not sufficient to predict sample volatility. According to Charlesworth (10), the relative volatilities of solutes can be assessed by comparing the temperatures at which a vapor pressure of 1-mm Hg is achieved. Some data about vapor pressures at different temperatures for the PACs studied are given in Tables V–VII together with the absolute response factors for the standards studied. In order to carry out relative comparisons between the most studied PACs, and given that volatility data are not available for many PACs and the different range of temperatures studied in each case, similar temperatures were chosen as often as possible. However, relative

long-chain alkanes or PAHs, and this is also in agreement with the mechanism of FID response.

In the case of polar fractions from heavy oils (Table VIII) and related materials, such as coal conversion products, it is important to take into account that "polarity" is a confusing and relative term. The "polar fraction" definition from a deasphalted petroleum oil does not necessarily imply the occurrence of the aforementioned type of PACs (with heteroatoms) in such a fraction. In the absence of heterocompounds (as is the case with some deasphalted products), and for a given MW, hydrogenated PAHs may present higher polarity (and consequently elute later) than their corresponding PAHs. Our results for these kinds of products are in fact very similar to those obtained for other fractions.

Conclusion

The TLC-FID technique exhibits an adequate performance on its own. Data are adequately fitted to logarithmic regressions in the whole mass range studied (0.1–12 μg) because deviations from linearity were found at sample loads lower than 1 μg . For the lowest mass range (< 1 μg), repeatabilities were worse than those obtained at higher sample loads. This should be considered when a quantitative analysis is to be done. For sample loads higher than 1 μg , linear regressions provided adequate regression coefficients and intercepts with low relative errors.

A particular capability of TLC-FID is the possibility of varying the scan speed. Absolute response factors obtained for different rubrene loads (a high-MW compound) did not significantly vary with scan speed, except in the case of the slowest speeds (i.e., 60 s/scan). In this case, smaller (although linear) signals were obtained. This could be used in order to inject higher sample loads in cases in which a given mass saturates the detector. According to our results, volatilization of rubrene prior to combustion should not take place.

Although volatility effects cannot be discarded, especially in the case of the smaller compounds, our data seem to support the hypothesis that differences in sensitivity for the slower scan speeds could also be caused by a more complete combustion of the sample and a smaller production of ions in the FID detector.

Although clear differences in response factors can be observed among different compounds and different scan speeds, the abso-

lute response factors are reasonably uniform for each homologous series of alkanes longer than C_{24} and aromatics with 4 or more rings.

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